SAS4302 Polymer Science Chapter 2 Molecular Weight

- Molecular weights in polymers are not a precise value
- Polymers are heterogeneous consisting of molecules of different lengths or sizes
- Unlike simple organic compounds, which have a precise, accurate molecular weight irrespective of method of separation or method of determination

So polymer molecular weights are average values

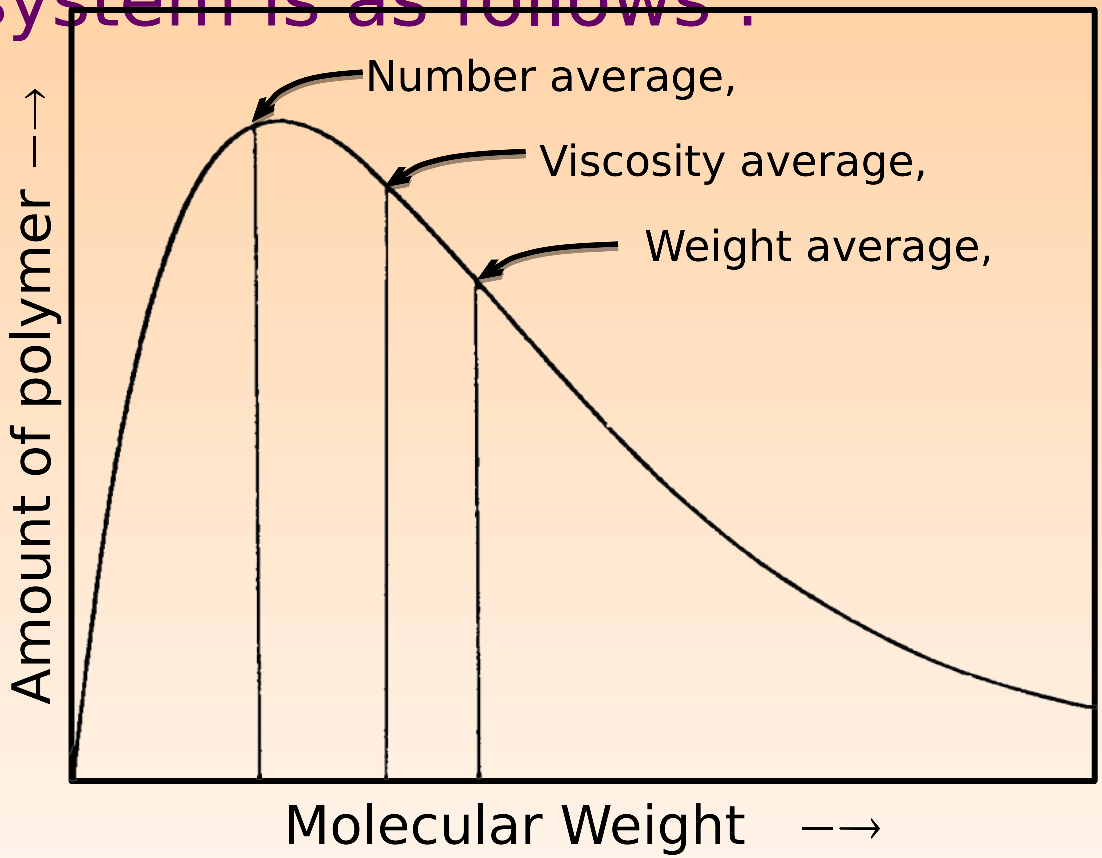
There are **<u>THREE</u>** types of average values

1. ***Number-average molecular weight M_n***
   – the total weight of polymer divided by the total number of molecules

2. ***Weight-average molecular weight M_w***
   – depends not only on the number of molecules present, but also on the weight of each molecule

3

Molecular weight distribution curve for a typical heterogeneous polydisperse system is as follows :



Distribution of molecular weight in a typical polymer

i.e. $M_w > M_v > M_n$

1. Number-average molecular weight,

= no. of molecules of i species

= molecular weight of molecules of species

2. Weight molecular weight,

3.Viscosity-average molecular weight ,

α is a constant for a given polymer-solvent system.

If $\alpha = 1$, then

(PS -Toluene : $\alpha = 0.62$ and $K = 3.7 \times 10^{-4}$)

is always greater than for polydisperse system

The ratio or is called the index of polydispersity (Dispersity factor)

It indicates how broad or narrow the molecular weight distribution is

Example

Polymer sample consists of

- 1 chain molecular weight 150,000
- 1 chain molecular weight 50,000
- 5 chains molecular weight 100,000.

Calculate , and the index of polydispersity.

Solution :

–

Solution :

–

Index of polydispersity:

$$= 1.07$$

- If one chain of 300,000 is now added to this mixture, then

$$= 125000$$

$$= 165000$$

Index of polydispersity:

$$= 1.32$$

- If , the polymer is monodisperse and is homogeneous
- It is an ideal case; it rarely happens in polymers

	Distribution
<5	narrow
5-20	medium
>20	broad

- For step growth polymer, ratio is normally small
- For example Nylon 6,6 it is often equal to 2
- However for chain growth polymer any number may be possible

Methods of determining molecular weight averages

1\.

a. <u>End group analysis</u>

End group analysis is mainly used for step growth polymers because they have end groups that are easily analyzed

e.g.

- $-NH_2$ and $-COOH$ in polyamides
- $-COOH$ and $-OH$ in polyesters
- $-OH$ and $-N{=}C{=}O$ in polyurethanes

Araldite – Epoxy Adhesive

Example (Ref : Acid Number)

- Suppose 1 g of an Epoxy (Araldite) adhesive is taken which is known to contain one -COOH group per polymer molecule. If 10.00 mL of 0.01M NaOH solution is needed to neutralize this sample, what is the molecular weight of the polymer ?

Solution

- no. of moles of NaOH used are $(10 \times 0.01)/1000 = 10^{-4}$ moles
- $\therefore$ no. of moles of -COOH groups $= 10^{-4}$ moles
- Since each polymer molecule contains one -COOH group, the no. of moles of polymer present $= 10^{-4}$ moles.

Con’t

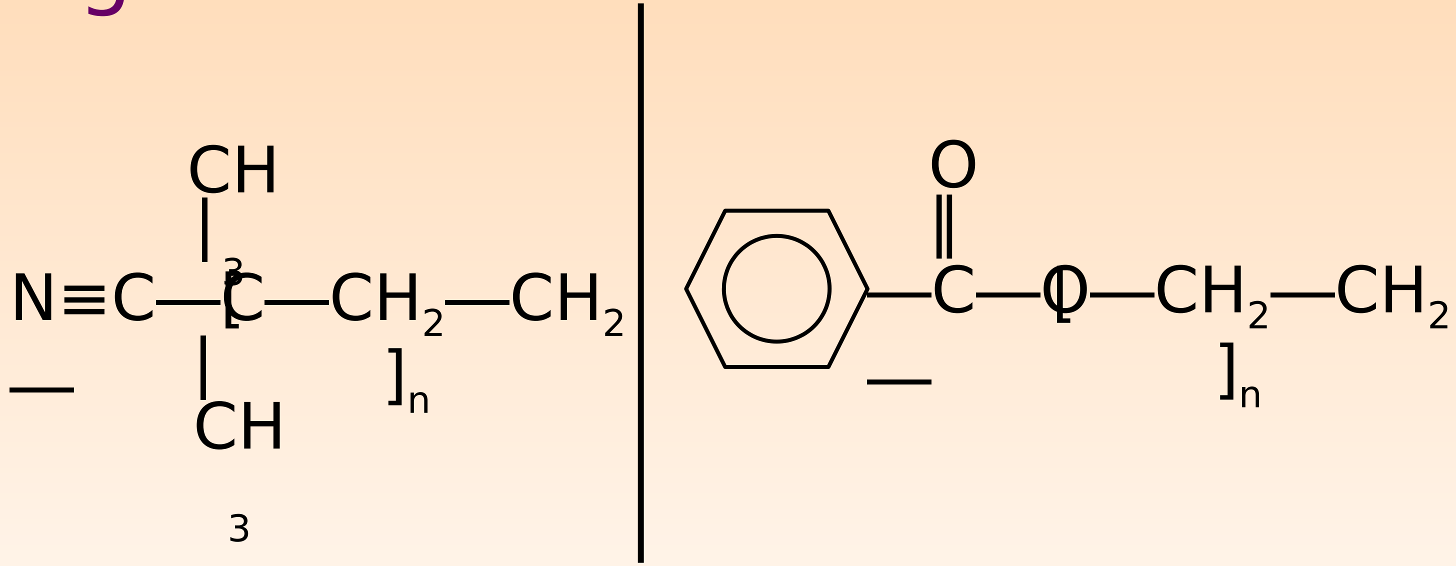
- But 10^{-4} moles of polymer weighs 1 g
- $\therefore$1 mole of polymer weighs $1/10^{-4} = 10^4$
- Since this method of end group analysis has involved counting the number of -COOH groups

$\Rightarrow$ the no. of polymer molecules present $\therefore$the number-average molecular weight of the polymer is 10,000

Limitations

- The end group analysis has an upper working limit, for , of ~25,000
- This method is useful for low relative molecular weight condensation polymers
- Other groups can be detected easily include -OH (in polyesters); $-NH_2$ groups (in polyamides)

- Chain growth polymers have end groups that are difficult to analyze
- e.g. initiator residues



- Due to higher molecular weight of chain growth polymers, there are few end-groups (low concentration) present in a given mass of polymer

b. Colligative properties of solutions

(□□□)

i. Depression of freezing point (Cryometry)

ii. Elevation of boiling point (Ebulliometry)

iii. Lowering of vapour pressure

Colligative properties are properties of solutions that depend on the *ratio of the number of solute particles to the number of solvent molecules* in a solution.

Colligative Properties

- Each of these can be measured for solutions of different *concentrations* and the results obtained depend on the total number of solute present in a fixed amount of solvent

- 1 mole solute in 1 litre water / benzene

i. 1.86°C / 5.0°C

ii. 0.52°C / 2.70°C

iii. 0.5 mm Hg

iv. 22.4 atmospheric pressure

Freezing Point Depression

Boiling Point Elevation

Lowering of vapor pressures

Osmometry

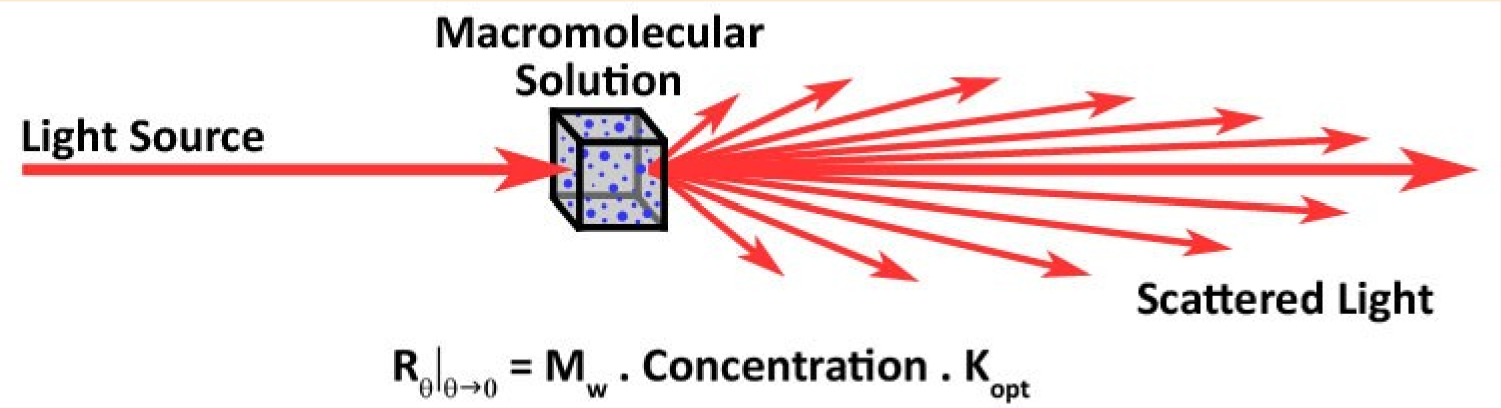
- For i and ii. ,
- The smaller the molecular weight the larger the change in temperature,

  ∴the higher the molecular weight the is so small which is difficult to detect

2.

a. <u>Light scattering</u>

Light scattering depends on the shape and size, the size depends on the molecular weight



b. Ultracentrifugation

- sedimentation equilibrium
- done in vacuum condition (~10^{-5} torr)
- very high speed spin
- use optical technique e.g. refractive index

  (note : 1 torr =1 mm Hg)

3.

- solution viscosity e.g. 1% polystyrene in toluene
- a U-tube viscometer

e.g.

a. Ostwald
b. Ubbelohde suspended-level or Dilution viscometer

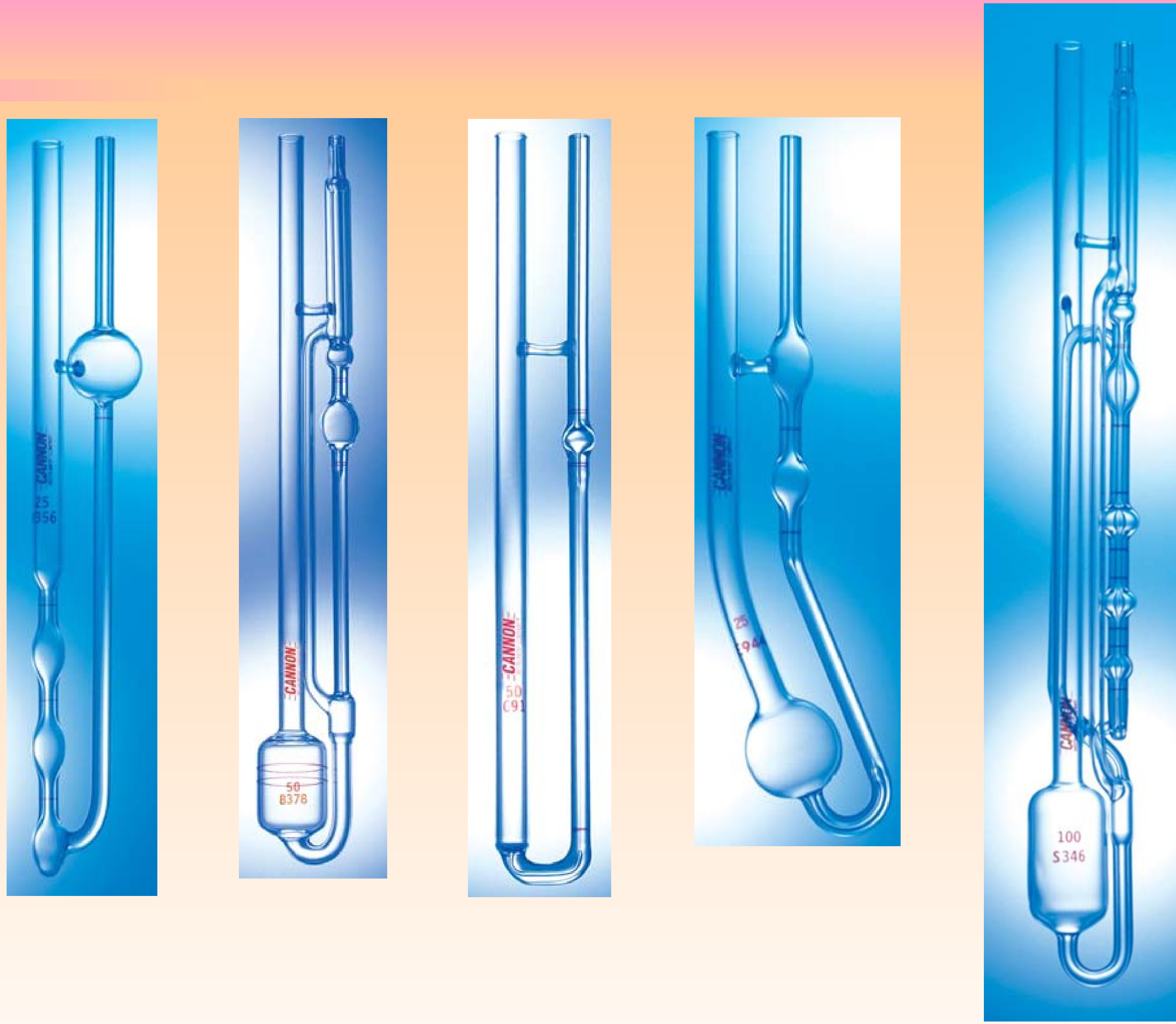
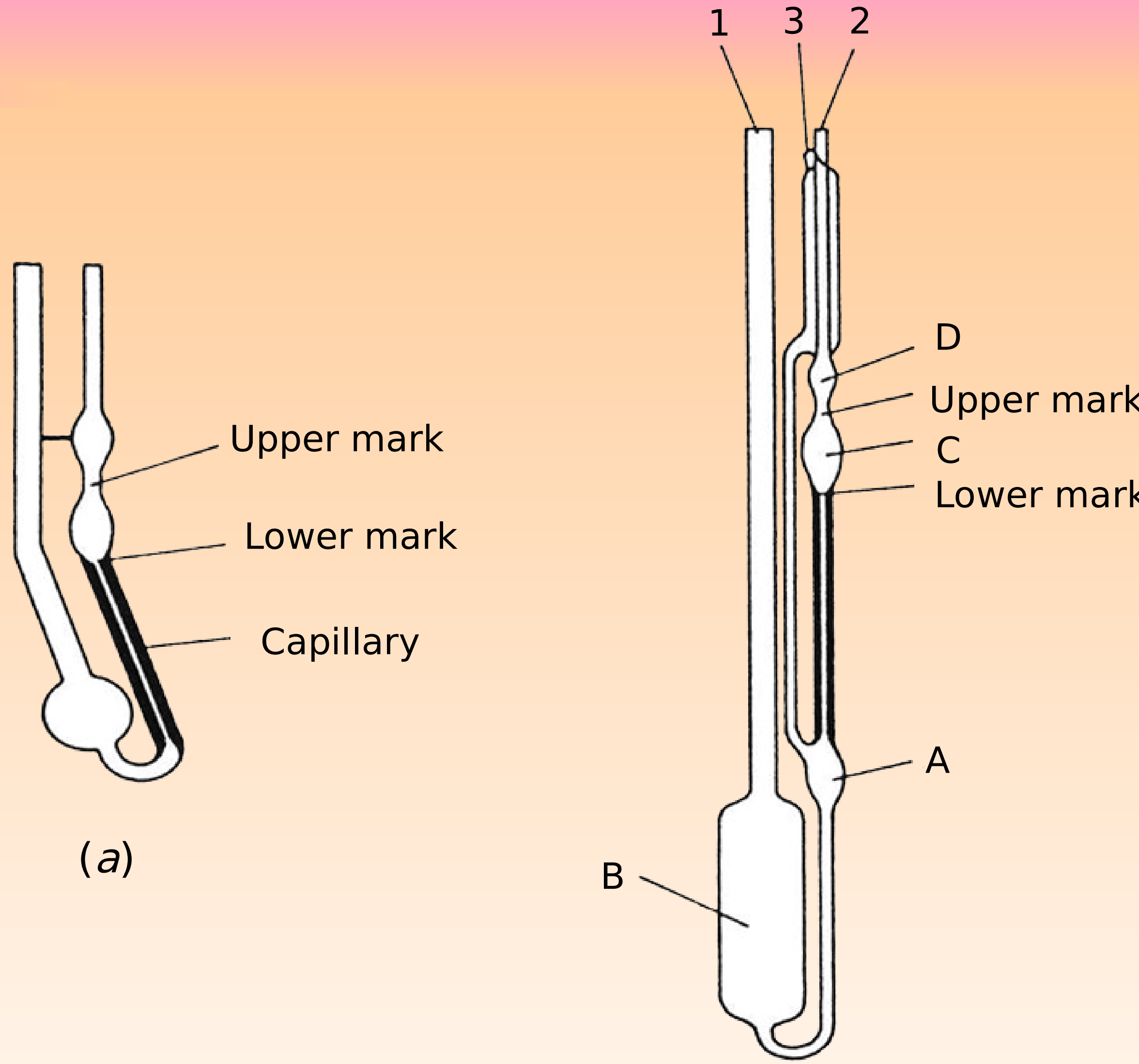


Figure 3.8 Common solution viscometers: (1) Cannon-Fenske Opaque, (2) Cannon-Ubbelohde Semi-Micro Dilution, (3) Cannon-Manning Semi-Micro, (4) Cannon-Fenske Routine, (5) Cannon-Ubbelohde Shear Dilution. (with permission from Cannon Instrument Company).



(b)

Capillary viscometers commonly used for measurement of dilute-solution viscosity: (*a*) Cannon-Fenske; (*b*) Ubbelohde

Advantages of Ubbelohde Viscometer over Ostwald Viscometer

i. It does not require to be filled with same volume of solution each time

ii. It is possible to carry out dilutions of the polymer solution in the viscometer itself

Advantages of viscosity methods

i. The experimental procedure is quick and easy
ii. The apparatus is cheap
iii. The calculation of results is simple

Disadvantages of viscosity methods

i. It is not an absolute method

ii. Each polymer system must be first calibrated with absolute molecular weight determinations (e.g. light scattering) run on fractionated polymer samples

iii. The concentration of the test sample is ~ 0.5 g /100mL solvent

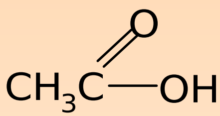
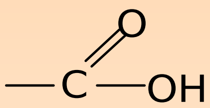
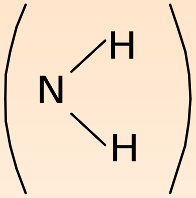
4. and

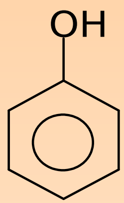
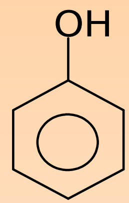
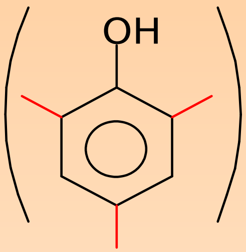
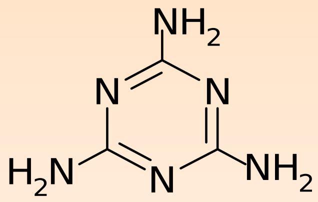
Gel Permeation Chromatography (GPC) or Gel Filtration or Size Exclusion

- modern instrument
- similar to High Performance Liquid Chromatography (HPLC)
- expensive
- for high molecular weight compounds, results can be got within several hours

Functionality

1. ***Functionality, f***
2. ***Extent of reaction, p***
3. ***Degree of polymerization,***
4. ***Carothers equation***

		Functional group	*Functionality, f*
1.	CH_3CH_2OH	—OH (1)	1
2.		 (1)	1
3.	$CH_3CH_2NH_2$	$—NH_2$ (1)	2 
4.	$HO—CH_2CH_2—OH$	—OH (2)	2

		Functional group	*Functionality, f*
5.			3 
6.		 (3)	6

1. *Functionality , f*

- The functionality of the monomer is the number of *reactive groups* present in a molecule and is normally known as ***f***

- Functionality is very important for step-growth polymerization

a. If monofunctional materials are used, low molecular weight products are formed

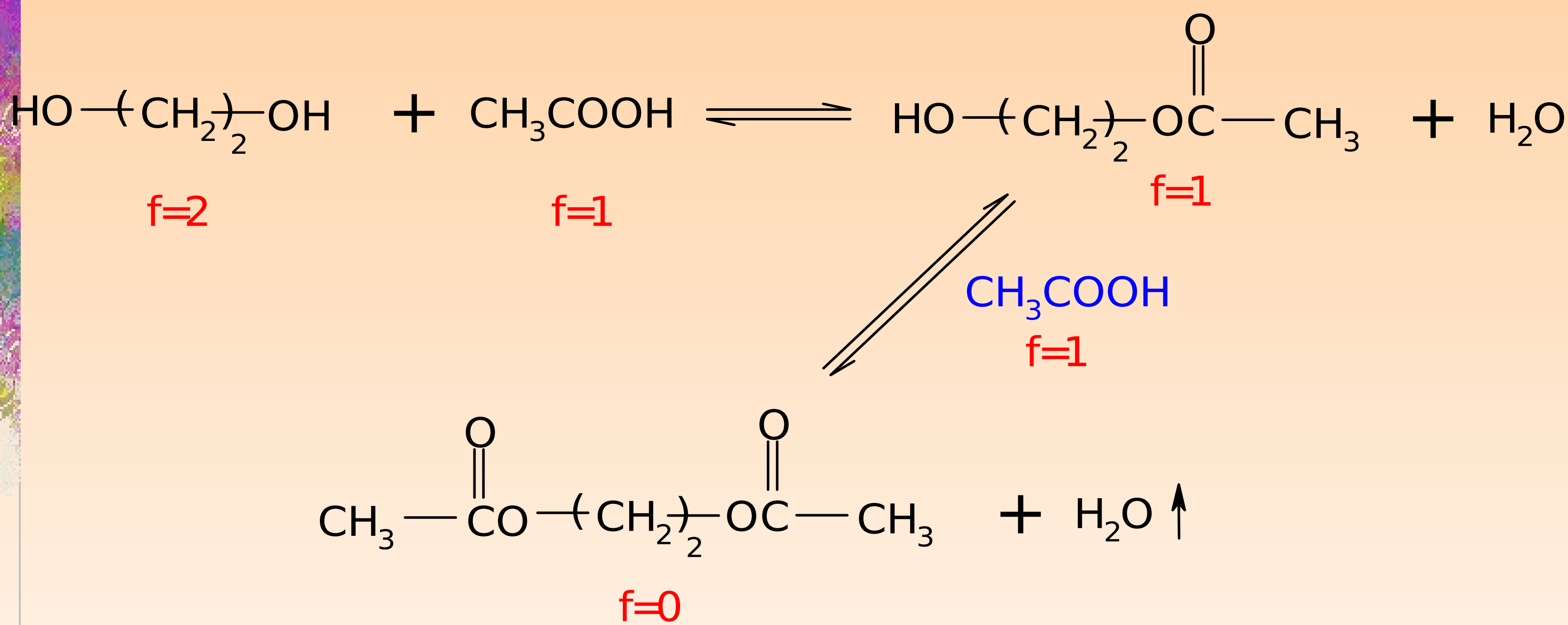
i. $$C_2H_5OH + CH_3COOH \rightleftharpoons C_2H_5O-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3 + H_2O$$

f=1 *f*=1 *f*=0

ii. $$RCOOH + R'NH_2 \rightleftharpoons RCONHR' + H_2O$$

f=1 *f*=2 *f*=1

iii

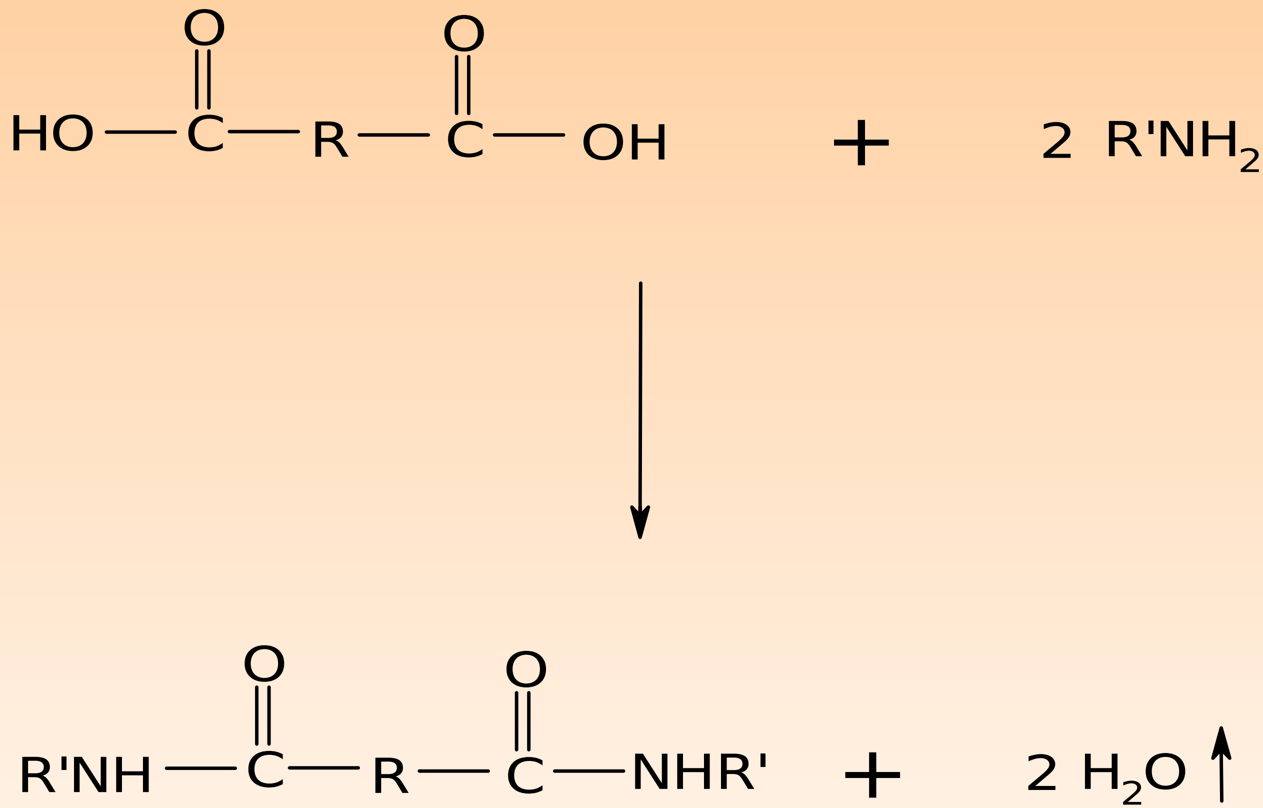


HO—(CH2)2—OH + CH3COOH ⇌ HO—(CH2)2—OC(=O)—CH3 + H2O
f=2
f=1
f=1
CH3COOH
f=1
CH3—C(=O)O—(CH2)2—OC(=O)—CH3 + H2O ↑
f=0

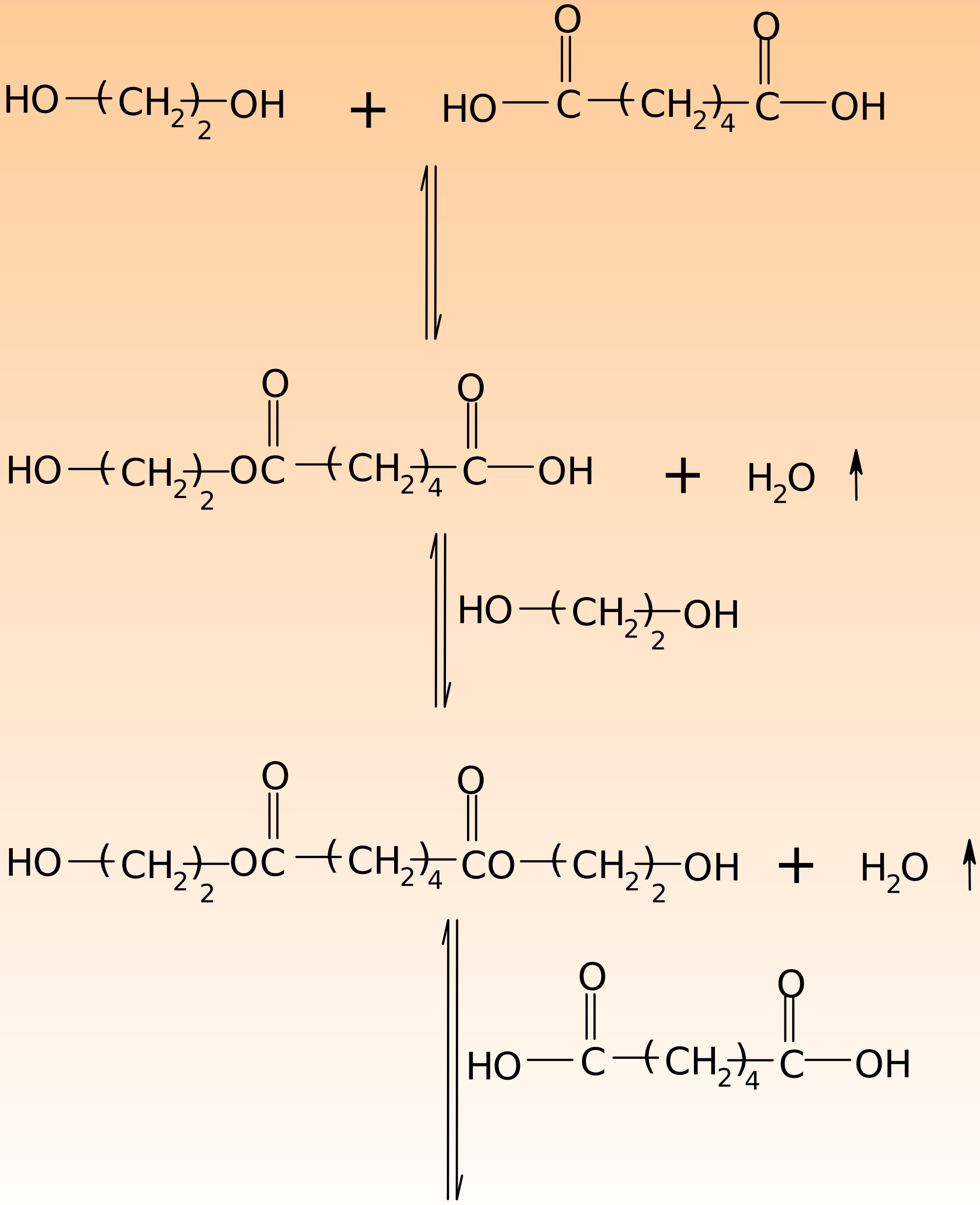
Whenever monofunctional material is present, the molecular weight is reduced or controlled

b. In order to make a high molecular weight linear polymers, the materials used should have a functionality of ***2***

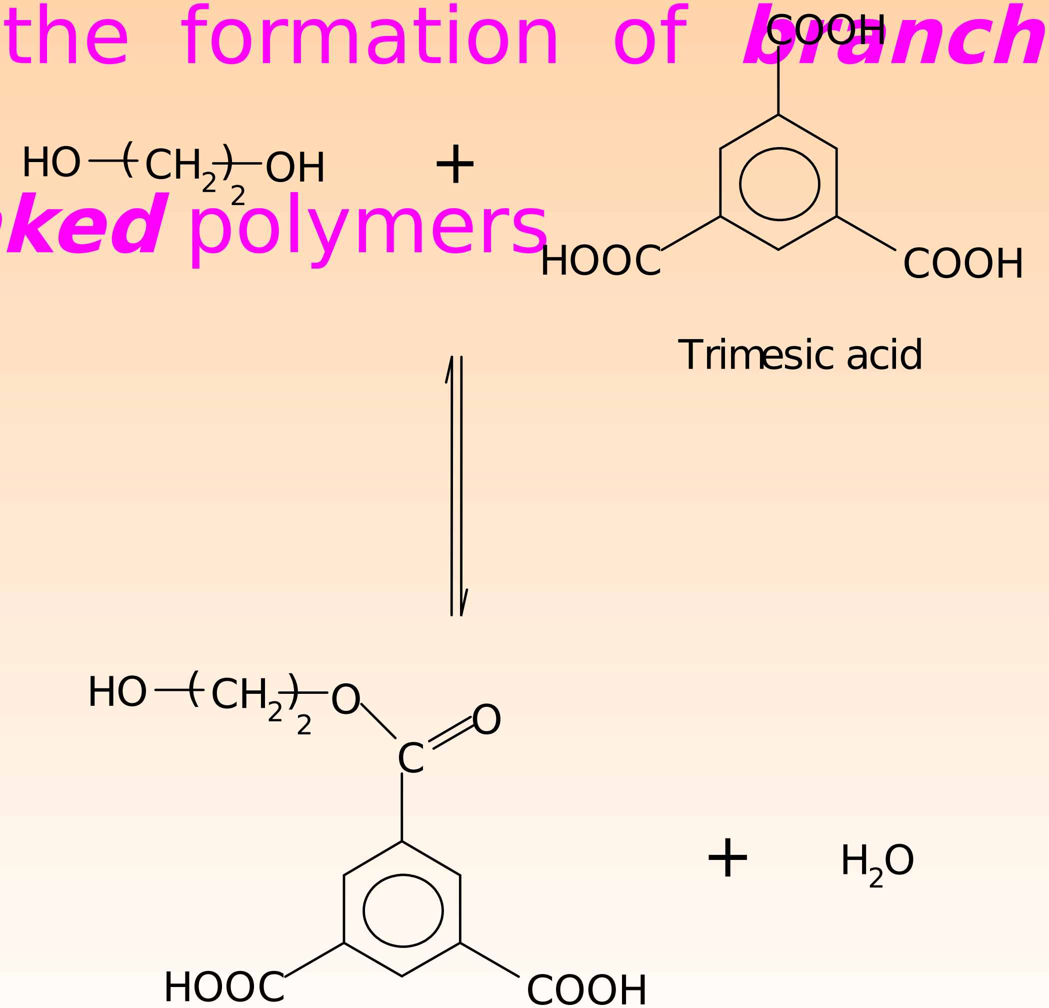
<i.>



<ii.>


HO—(CH2)2—OH + HO—C(=O)—(CH2)4—C(=O)—OH
HO—(CH2)2—OC(=O)—(CH2)4—C(=O)—OH + H2O
HO—(CH2)2—OH
HO—(CH2)2—OC(=O)—(CH2)4—C(=O)O—(CH2)2—OH + H2O
HO—C(=O)—(CH2)4—C(=O)—OH

c. Materials with functionality greater than 2 lead to the formation of ***branched*** and ***crosslinked*** polymers



Addition of monofunctional material will control the molecular weight of the polymer

$$x\,\mathrm{HOOC{-}R{-}COOH} \;+\; x\,\mathrm{H_2N{-}R'{-}NH_2} \;+\; y\,\mathrm{R''COOH}$$

$$\downarrow$$

Product

$$\mathrm{R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\overset{\overset{\displaystyle H}{|}}{N}{-}R'{-}\overset{\overset{\displaystyle H}{|}}{N}{-}\left(\overset{\overset{\displaystyle O}{\|}}{C}{-}R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\overset{\overset{\displaystyle H}{|}}{N}{-}R'{-}\overset{\overset{\displaystyle H}{|}}{N}\right){-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R''}$$

Average functionality () of a system $[M_1, M_2]$

=

=

Calculate the average functionality of

1. 10 HOOCRCOOH + 10 HOR'OH
2. 10 HOOCRCOOH + 10 HOR'OH + 10 R"COOH
3. 10 HOOCRCOOH + 10 HOR'OH + 10 $C_6H_3(COOH)_3$

e.g.

1. 10 HOOCRCOOH + 10 HOR'OH

$$\text{Average functionality} = \frac{2 \times 10 + 2 \times 10}{10 + 10}$$

$$\bar{f} = 2$$

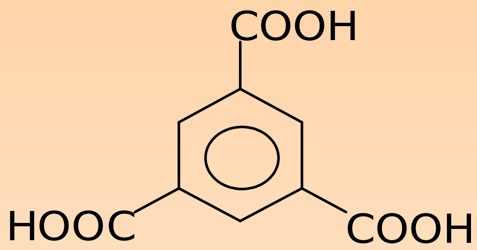
2. 10 HOOCRCOOH + 10 HOR'OH + 10 R''COOH

$$\text{Average functionality} = \frac{2 \times 10 + 2 \times 10 + 1 \times 10}{10 + 10 + 10}$$

$$\bar{f} = 1.67$$

e.g.

3.

10 HOOCRCOOH + 10 HOR'OH + 10 

$$\text{Average functionality} = \frac{2 \times 10 + 2 \times 10 + 3 \times 10}{10 + 10 + 10}$$

$$\overline{f} = 2.33$$

Summary

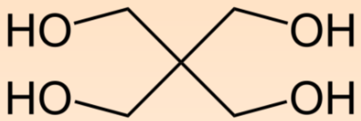
- ***f* < 2**, low molecular weight products, due to presence of monofunctional compounds

- ***f* = 2**, high molecular weight linear polymers. The raw materials for producing the polymers should have the purity of > 99.9% since the purity will seriously affect the molecular weight of the polymers

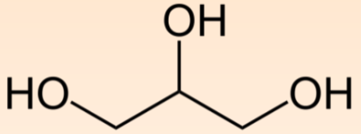
Summary

- ***f* >2**, high molecular weight crosslinked polymers formed due to presence of monomers with functionality of 3 or more

e.g. pentaerythritol



glycerol



Exception

A monomer must not simply bifunctionality ($f = 2$), but the ability to form 2 or more bonds to other monomers

e.g. 6-amino hexan-1-ol

$$HO—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—NH_2$$

It is bifunctional

It does not form a polymer, because its functional groups do not react with each other

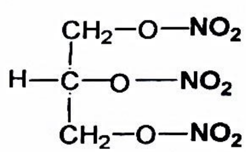
- Conversely, ethylene is monofunctional
- It can produce a polymer, because it can form 2 bonds to other monomers, the π bond being converted into 2 halves of 2 σ bonds

$$n\ CH_2{=}CH_2 \longrightarrow \left[-CH_2-CH_2- \right]_n$$

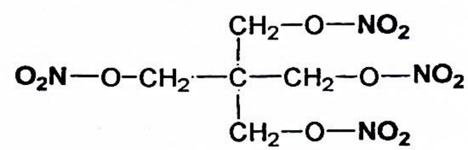
PETN（pentaerythritoltetranitrate）是另一個晚近發展出來的爆炸物質，很遺憾卻淪爲恐怖分子的新寵。PETN 與橡膠混合可以製造出所謂的**塑膠炸藥**，它的特色是可以塑造成任何形狀。PETN 的化學名稱聽來複雜，但它的結構並不然，其化學性質與硝化甘油非常相似，只不過它具有五個碳原子（硝化甘油有三個），並多了一個硝基。

[12] 一九九三年二月二十六日，恐怖分子在紐約世貿大樓外側引爆汽車炸彈，造成六人喪生，一千多人受傷。紐約世貿大樓已於二〇〇一年的九一一攻擊事件中化為灰燼。

[13] 一九九五年四月十九日，一輛滿載炸藥的卡車在奧克拉荷馬市的聯邦大樓引爆，造成包括十九名兒童在內的一六八人喪生，六七四人受傷。主嫌麥克維為美國激進派，已於二〇〇一年伏法。此爆炸案為美國本土傷亡第二慘重的不幸事件。

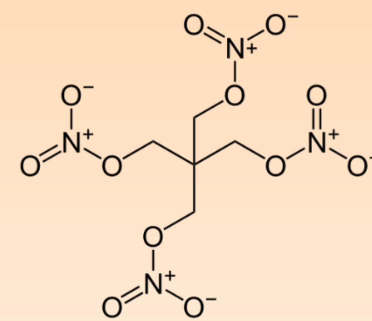


硝化甘油



PETN

（以粗體即為硝基）



PETN 容易引燃、對震動敏感、威力強大，也幾乎沒有氣味，即使是訓練有素的防爆犬，也很難偵測出來，因此常被恐怖分子做成飛機炸彈。其中最讓人印象最深刻的例子，就是一九八八年泛美航空 103 班機在蘇格蘭洛克比上空爆炸，並造成二百七十人罹難的悲劇，當時曾於飛機殘骸中發現 PETN 的成分。[14] 還有一次是著名的〝鞋子炸彈客〞事件。[15] 一名自巴黎搭乘美國航空班機的乘客，意圖引爆藏於鞋底的 PETN，所幸機組人員與乘客機警制伏，避免一場可能發生的悲劇。

2. Extent of reaction, p

- The extent of reaction, **p**, is the number of monomer units which have reacted

- Normally it is expressed as a *percentage* of the originally monomer available

(moles) present after time ***t***

no. of molecules (moles) which have reacted

= and

- If **p** = 0.99 or 99%, it means that 99% of the monomers have been used up

3. Degree of polymerization ,

- Degree of polymerization of all polymer molecules in any system is simply the original number of molecules (**N**$_o$) divided by the number of molecules at the end of reaction (**N**)

i.e. =

- Degree of polymerization of chain-growth polymer of a single polymer chain is the number of monomer units connected together to form a polymer

e.g.

$$x\,CH_2 = CH_2 \; ------\rightarrow \; x/y\,(R—CH_2—CH_2—R)_y$$

(N_0) (N)

Thus, = = = y

If $\boldsymbol{x} = 1000$, $\boldsymbol{y} = 1000$

i.e. $\mathbf{N}_o = \boldsymbol{x} = 1000$, $\mathbf{N} = \boldsymbol{x}/\boldsymbol{y} = 1$

$\therefore = \mathbf{N}_o/\mathbf{N} = 1000 = \boldsymbol{y}$

If $\boldsymbol{x} = 1000$, $\boldsymbol{y} = 500$

i.e. $\mathbf{N}_o = \boldsymbol{x} = 1000$, $\mathbf{N} = \boldsymbol{x}/\boldsymbol{y} = 2$

$\therefore \; = \mathbf{N}_o/\mathbf{N} = 500 = \boldsymbol{y}$

***

- ***Molecular weight = M_r x DP (i.e. y) , where M_r is the molecular weight of monomer***

Exercise

If for polypropylene is 252,000, what is its ?

Hint:

$$nCH_2{=}CHCH_3 \longrightarrow R\text{-}(CH_2CHCH_3)_n\text{-}R$$

Solution

- Molar mass of propylene = 42
- therefore = 252,000/42

  = 6000

4. Carothers equation

Relationship between DP and p is known as Carothers equation

$\Rightarrow$DP = 1/(1 - **p**), applies to ***step-growth polymerization (condensation) ONLY***

e.g.

- **p** = 50% , DP = 1/(1 - 0.5) = 2
- **p** = 95% , DP = 1/(1 - 0.95) = 20
- **p** = 98% , DP = 1/(1 - 0.98) = 50
- **p** = 99.99% , DP =1/(1 - 0.9999) = 10,000

- In a single polymeric molecule, DP is the number of monomers joined together
- But in most polymers, a mixture of different molecular size is obtained so DP is an average value

Example 1

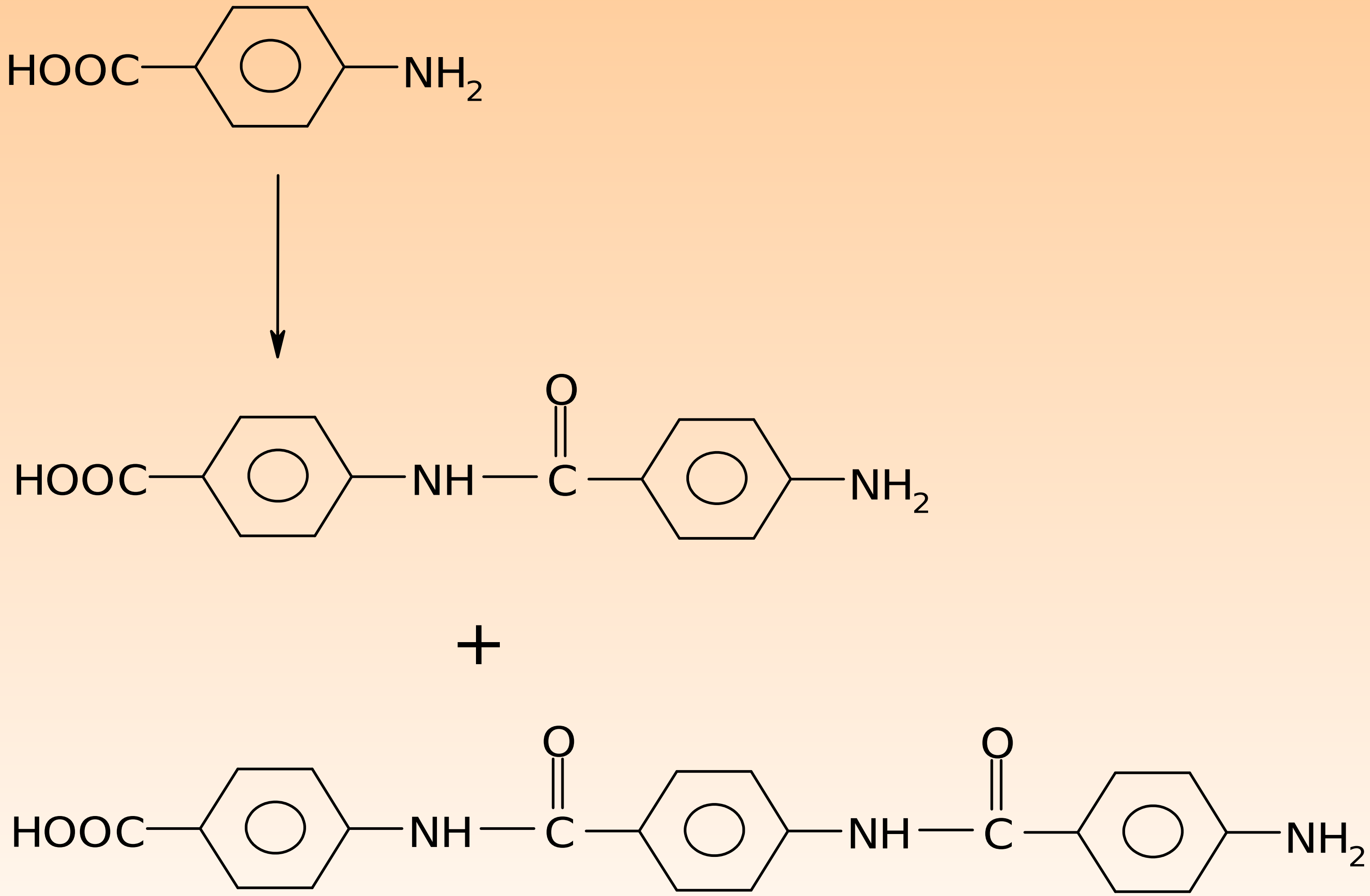
$100\ M_o \dashrightarrow [M_o]_{20} + [M_o]_{25} + [M_o]_{10} + [M_o]_{30} + [M_o]_{15}$

average = 20

$N_o = 100, \quad N = 5$

average = 20

Example 2

5 

or

or